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Optical dephasing in organic amorphous systems. A photon echo and hole-burning study of pentacene in polymethylmethacrylate

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Picosecond photon echo experiments on pentacene in polymethylmethacrylate (PMMA) show that the homogeneous width exhibits a $T^{1.3}$ temperature dependence. This behavior is ascribed to coupling of the pentacene transition to randomly distributed low-frequency excitations in the amorphous host. A calculation of the resulting homogeneous width is presented which uses optical Redfield theory as a starting point. From the results of this calculation we conclude that the coupling between the pentacene molecule and the host low frequency excitations is of static dipolar nature and that the density of states of these excitations varies as $\omega^{0.3}$. Results of nonphotochemical hole-burning experiments on the same system are also reported. Comparison of these results with the ones obtained by the photon echo method indicates, that in the hole-burning experiments, the hole width and its temperature-induced broadening are dominated by spectral diffusion.

INTRODUCTION

In recent years photoinduced hole burning[1–4] and picosecond photon echoes[5–8] have been successfully used to elucidate the mechanism of optical dephasing in electronic transitions of molecules in crystalline solids. It was found that in the case of deep traps in chemically mixed crystals, the guest librations are the doorway states in coupling the electronic excitation to the host lattice vibrations. Following the initial work by van't Hof and Schmidt on spin[9] and the work by Harris *et al.*[10] on vibrational dephasing, de Bree and Wiersma (dBW)[11] used optical Redfield theory to describe libration-induced dephasing of electronic transitions in molecular crystals. De Bree and Wiersma showed that there are two distinct ways in which librations can affect optical coherence depending upon whether or not the cold and librationally hot transitions spectrally overlap. These limiting cases known, respectively, as the exchange[9,10] and the UPS[11] model have recently convincingly been demonstrated.[4,7] It therefore seems that our present understanding of optical dephasing in molecular crystals is satisfactory.

More limited, however, is our present understanding of optical dephasing in amorphous solids. Pioneering work in this area was done by Selzer *et al.*[12] for inorganic glasses and by Small's group[13] for organic amorphous systems. Selzer *et al.*[12] employed fluorescence line narrowing and Small *et al.*[13] nonphotochemical hole burning as a tool to obtain information on the temperature dependence of the optical dynamics in these systems. No universal trend was observed by them or others except that the coherence decay, over a certain temperature range, could be fit to the functional form T^{γ}, where γ, different from case to case, varied between 1 and 2.2.[14–17] Both aforementioned groups suggested that this "anomalous" temperature dependence was induced by the disorder present in amorphous systems. This idea was worked out is detail in papers by Lyo and Orbach[18] for inorganic and by Small and co-workers[14] for organic glasses. Despite the progress that was made at the time in understanding the basic phenomenon underlying the anomalous optical dynamics in amorphous systems, several questions remained. In particular in the case of organic amorphous systems the observed large disparity between the measured low-temperature nonphotochemical hole width and the calculated lifetime-limited width seemed suspect. At this point in time it was shown by the Voelker group[19] that, with the technique of photochemical hole burning, much narrower holes were obtained which, at very low temperature (0.3 K), became close to lifetime limited. With this technique, the Voelker group found in many organic amorphous systems a $T^{1.3}$ dependence for the optical dephasing constant, suggesting that for this class of materials a single dephasing mechanism is operating. Recently the same $T^{1.3}$ temperature dependence was measured, using photon echoes, for optical dephasing in an inorganic glass below 1 K.[20]

On the theoretical side there has also been substantial activity following the first publication by Selzer *et al.*[12] on the subject. All theories presented have in common that they rely on the presence of tunneling modes, a conjecture first made by Anderson *et al.*[21] and independently by Phillips.[22] These authors invoked the presence of these modes in order to explain the observed[23] anomalous heat capacity and conduction in amorphous systems at low temperature. While, as stated, all theories describing optical dephasing in amorphous systems also assume the presence of low frequency modes, they differ in either the assumed coupling between the optical transition and low frequency modes or in the statistical averaging procedure used to account for the spatial and energy distribution of these tunneling modes.

In a formal sense, the assumption of the presence of tunneling modes, which act as doorway states in the process of optical dephasing, appears to be very similar to the case of a crystalline solid where low-frequency guest librations are strongly coupled to the optical transition. One therefore expects that, aside from statistical averaging, the optical Redfield relaxation theory developed by dBW[11] should be applicable. In this paper we will show that this is indeed so, and

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present the relevant Hamiltonian in such a way that it is isomorphous to the one used by dBW. We will then use their formal results to describe optical dephasing in an amorphous host system. Our final expression for the homogeneous width is in general agreement with the one recently derived by Lyo[24] using a Green's function method.

On the experimental side we report results of picosecond accumulated photon echo and nonphotochemical hole-burning experiments on the system pentacene in the (amorphous) polymer polymethylmethacrylate (PMMA). In contrast to the results obtained by Macfarlane and Shelby[25] in a recent photon echo and hole-burning study of the inorganic Pr^{3+}/silicate glass, our results obtained with the different techniques are not compatible. We conclude that the hole width measured with the hole-burning method is dominated by spectral diffusion. From the photon echo experiments we derive that, in the temperature range between 1.5 and 12 K, the homogeneous linewidth is activated as $T^{1.3}$, supporting the results obtained by the Voelker group for different molecules in the same polymer,[19] but using photochemical hole burning as a technique. On the basis of the observed $T^{1.3}$ functional form for the homogeneous linewidth we conclude from our theoretical model that (static) dipolar coupling between pentacene and randomly distributed tunneling systems provides the main source for the effect of phonon assisted tunneling on optical dephasing. With this assertion the density of states function for the tunneling systems is found to vary as $\omega^{0.3}$.

THEORETICAL BACKGROUND

Optical dephasing by coupling to tunneling modes

In this section we calculate the expected homogeneous width of an optical transition of a molecule embedded in an amorphous system. Before doing so, we must question the possible role of librations in the optical dephasing process in an amorphous system. Molecular librations obviously exist in such systems be it that their frequencies will be very much site dependent. The main argument against a role from librations in the dephasing process stems from the fact that in all crystalline systems studied so far, its contribution to the homogeneous width becomes negligible at low temperature (1.5 K) and the width becomes lifetime limited. In amorphous systems at this temperature, dephasing can still be orders of magnitude faster than given by the population relaxation time. This suggests that the optical excitation is strongly coupled to other low-frequency excitations in the host. We suggest that libration induced dephasing in amorphous systems is absent because of the strong coupling of the molecular librations to the glass acoustic vibrational modes. Consequently the librational lifetime will become very short which enables coherence exchange effects to "average out" the effect of phonon scattering processes involving these librations (Refs. 9–11, *vide infra*). Following previous theoretical efforts[14,18,24,26–30] concerning this problem we will assume that an amorphous system contains a large number of low-frequency excitations, the so-called tunneling modes or two-level systems (TLSs), which are held responsible for the anomalously large homogeneous widths observed in these materials. First we consider the interaction between an optical excitation and one TLS and consider its dephasing characteristics. Then we calculate the appropriate average over the spatial and energy distribution of the TLSs.

Assuming that out of the phonon bath there are certain special levels (TLSs) that strongly interact with an optical excitation it seems appropriate to deal with those levels on an equal footing with the electronic states of the molecule considered. We can project these TLSs out of the bath and include them in the molecular Hamiltonian (H_A). The total Hamiltonian is then arranged as follows:

$$H = H_A + H_R + V_{AR}, \tag{1}$$

where H_A describes the optical excitations of the system "dressed" with the interaction with a TLS, H_R is the operator representing the anharmonic phonon bath and V_{AR} describes the coupling between the dressed molecular excitations and the phonon bath.

Reineker *et al.*[27] have recently given a detailed derivation of H_A which in the notation of the dBW paper[11] can be presented as

$$H_A = \sum_i \Big[\tilde{\epsilon}^i + \sum_\kappa F^i_{\kappa\kappa}(\bar{n}_k + \tfrac{1}{2}) + \hbar(\Omega + \Delta\Omega^i)B^+B \Big] a_i^+ a_i, \tag{2}$$

where $a_i^+(a_i)$ and $B^+(B)$ are the creation (annihilitation) operators for an electronic state i with energy ϵ_i (the index g denotes the electronic ground state), and a TLS excitation, respectively.

$$\tilde{\epsilon}^i = \epsilon^i - V^i,$$

$$\hbar\Omega = 2V^g,$$

and

$$\hbar(\Delta\Omega^i) = 2(V^i - V^g) \tag{3}$$

with

$$V^i = [(E/2)^2 - V_i\Delta + V_i^2]^{1/2},$$

thus V_i represents the interaction between a TLS and state i of the molecule, and $E = (\Delta_0^2 + \Delta^2)^{1/2}$ the tunneling splitting were Δ_0 is the energy difference in zero order between the two wells and Δ the interaction across the barrier. The second term in Eq. (2) represents a renormalization shift, due to the thermal average of coupling with the band phonons,[11] which is irrelevant to the following discussion. The explicit form of H_R and V_{AR} will not be given and plays no (explicit) role in the discussion.

The level scheme that belongs to H_A is presented in Fig. 1, where the potential wells are only included to remind the reader of the history leading to the four-level system.

The same level scheme as presented in Fig. 1 was used by dBW[11] to describe libration-induced dephasing in molecular mixed crystals. Instead of projecting the TLS mode out of the bath, as is done in amorphous systems, dBW, in molecular crystals, projected the librational mode out of the bath. They further used the same partition of the Hamiltonian as in Eq. (1) to describe optical dephasing induced by phonon scattering processes involving the guest librations. As the "molecular" Hamiltonain (H_A) in Eq. (2) used to describe

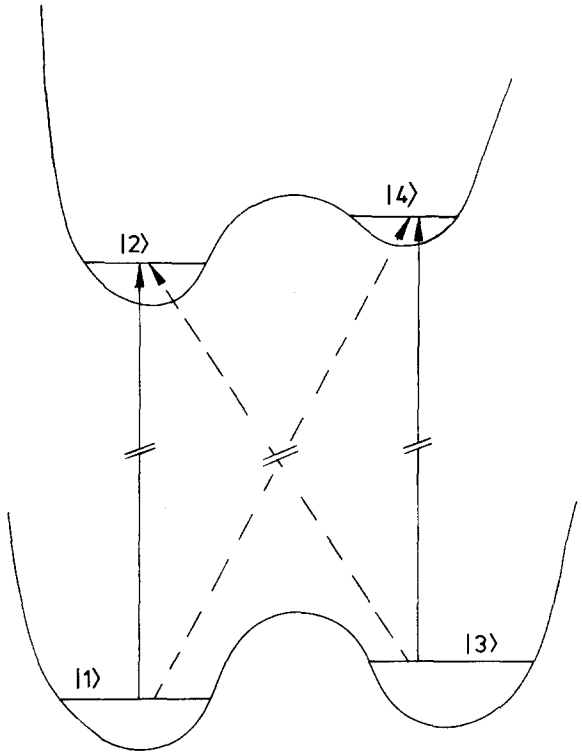

FIG. 1. Four-level model system arising from the interaction between an optical transition and a two-level system projected out of the phonon bath of an amorphous solid. The solid and broken lines indicate allowed and forbidden optical transitions, respectively.

optical dephasing in a glass is isomorphous to the one previously used to describe libration-induced dephasing we can immediately use the results of the dBW paper to calculate the expected dephasing for the level system of Fig. 1. Before doing so we note the following: in the case of a mixed molecular crystal, where levels 3 and 4 represent librational states, we were able to excite all the indicated transitions in Fig. 1 (assuming they have osillator strength) separately and measure their dephasing characteristics. In an amorphous host, the inhomogeneous broadening can easily exceed the energy difference between levels 3 and 1 and 4 and 2 which implies that the coherence decay of all transitions is measured (solid and broken lines in Fig. 1) simultaneously. An interesting implication of this point is that even at 0 K we expect a contribution to the homogeneous linewidth from phonon relaxation processes on the diagonal transition $4 \leftarrow 1$, involving a "flip" in the TLS. However in all dephasing experiments performed on molecules in organic glasses so far, it seems that at very low temperature (0.3 K) the homogeneous width converges to a lifetime limited value.[19] This implies that the oscillator strength of the "flip" transitions is small compared to that of the allowed transitions, and for the purpose of a dephasing description only the vertical transitions have to be taken into account. The same selection rules were also imposed on the four-level system used by dBW to describe librational dephasing. In terms of the Hamiltonian in Eqs. (2) and (3) the implication is that $\Delta \gg V_i$ which leads to

$$(\Delta\Omega^i) = \frac{2\Delta\,(V_i - V_g)}{E}. \tag{4}$$

In the dBW theory of optical dephasing it is assumed that, on the time scale of the experiment, the detailed balancing condition holds for phonon scattering processes among the levels 1 and 3 and 2 and 4. With this assumption the only parameters that determine the homogeneous line shape under slow passage conditions (no saturation effects) are the rates *out* of levels 3 and 4, $\Gamma_{3\to1}(T)$ and $\Gamma_{4\to2}(T)$, respectively, the energy splittings $\hbar\omega_{31}$ and $\hbar\omega_{42}$ and an interference term ($\Gamma_{34\to12}$) which is only important when the cold and hot optical excitations overlap spectrally. In either case the line shape function is determined by $\mathrm{Im}[(\tilde\rho_{12}+\tilde\rho_{34})\mu]$, where $\tilde\rho_{12}$ and $\tilde\rho_{34}$ are the off-diagonal elements of the density matrix in the rotating frame and μ is the transition dipole. An explicit expression for $(\tilde\rho_{12}+\tilde\rho_{34})$ is given in Eq. (4.2) or the dBW paper[11] which, when appropriately averaged over the spatial and energy distributions of the TLSs, would lead to the desired line shape function of an optical transition in an amorphous host. This calculation not only presents a formidable task but also requires information on the dependence of the interference term ($\Gamma_{34\to12}$) on the distance between the molecule and a TLS. As this latter information is lacking we have, instead of using the exact expression, worked with the two limits of the general relaxation theory: the UPS and exchange limit. The procedure is then to calculate the line shape function of a transition in either the UPS or exchange limit and then take the appropriate (spatial) average by using the exchange condition.

In the UPS case, where the transitions $2 \leftarrow 1$ and $4 \leftarrow 3$ are spectrally distinct the line shape function becomes

$$\mathrm{Im}(\tilde\rho_{12}\mu) + \mathrm{Im}(\tilde\rho_{34}\mu). \tag{5}$$

The pure dephasing (T_2^*) constants for the cold (a) and hot (b) transitions are then given by

$$1/T_{2a}^* = \tfrac{1}{2}[\Gamma_{3\to1}(T)e^{-\hbar\omega_{31}/kT} + \Gamma_{4\to2}(T)e^{-\hbar\omega_{42}/kT}], \tag{6a}$$

$$1/T_{2b}^* = \tfrac{1}{2}[\Gamma_{3\to1}(T) + \Gamma_{4\to2}(T)]. \tag{6b}$$

The interpretation of Eqs. 6 is that the pure dephasing at each transition is determined by the "uncertainty width" of each level caused by the phonon scattering processes.

The pure dephasing contribution to the measured homogeneous width resulting from the UPS process will thus be given by

$$[\pi T_2^*(T)]_u^{-1} = \pi^{-1}(P_1/T_{2a}^* + P_3/T_{2b}^*)^{-1}, \tag{7}$$

where P_1 and P_3 are the populations of levels 1 and 3 at temperature T. With a random distribution in splitting energies ω_{31} and ω_{42}, the UPS contribution to the homogeneous width may also be expressed as

$$[\pi T_2^*(T)]_u^{-1} = \pi^{-1}\Gamma(\omega,T)(1+e^{+\hbar\omega/kT})^{-1}, \tag{8}$$

where $\Gamma(\omega,T)$ is the scattering rate out of the upper levels of the pairs in Fig. 1. Equation (8) is identical to the expression used by Lyo[24] to calculate the homogeneous width of an optical transition in a glass, showing that the Redfield formalism used in the dBW paper is equivalent to the Green's function approach used by Lyo.

When the cold and hot optical transitions spectrally overlap *and* the lifetimes of levels 3 and 4 are identical, the dBW theory arrives[11] at the well-known exchange expres-

sion for the pure dephasing contribution to the homogeneous linewidth:

$$[\pi T_2^*(T)]_e^{-1} = \frac{\pi^{-1}\delta^2\Gamma^{-1}(\omega,T)}{1+\delta^2\Gamma^{-2}(\omega,T)}\, e^{-\hbar\omega/kT}. \tag{9}$$

Note that the exchange equation is only applicable[11] in the limit where $\delta\Gamma^{-1}(\omega,T)\leqslant 1$. In the exchange expression, $\Gamma(\omega,T)$ is the downward rate for phonon scattering processes (from state 3 to 1 and 4 to 2) and δ and ω are defined as follows: $\delta = |\omega_{31} - \omega_{42}|$; $\omega = \frac{1}{2}(\omega_{31} + \omega_{42})$. It is clear from the exchange expression that the dephasing rate in the exchange limit is considerably reduced compared to the UPS limit and in the limit of very weak impurity–TLS interaction ($\delta \approx 0$) the exchange contribution to the linewidth vanishes.

The homogeneous linewidth in this approach will therefore have two contributions: an UPS from the few strongly coupled, and an exchange from the abundant weakly coupled TLSs. The critical distance (R_c), at which exchange takes over from UPS[11] can be calculated from the condition:

$$\delta(R_c)[\Gamma(\omega,T)(1+e^{-\hbar\omega/kT})] \approx 1. \tag{10}$$

The homogeneous width, $\Delta\omega_h$, may then be expressed as follows:

$$\begin{aligned}\Delta_{\omega h} = \langle\langle[\pi T_2(T)]^{-1}\rangle\rangle &= (2\pi\tau_{fl})^{-1} + \pi^{-1}\int_0^\infty d\omega\,\rho(\omega)\\ &\times\Bigg[\left\langle\int_{r_{\min}}^{R_c} d^3r\,\Gamma(\omega,T)(1+e^{\hbar\omega/kT})^{-1}\right\rangle\\ &+\left\langle\int_{R_c}^{\infty} d^3r\,\delta^2\Gamma^{-1}(\omega,T)\right.\\ &\left.\times(1+\delta^2\Gamma^{-2}(\omega,T))^{-1}e^{-\hbar\omega/kT}\right\rangle\Bigg],\end{aligned} \tag{11}$$

where τ_{fl} is the fluorescence lifetime, $\rho(\omega)$ the density of states function for the TLSs, $r_{\min}$ the minimum allowed distance between a molecule and a TLS, and $\langle\rangle$ indicates averaging over the TLS parameters Δ_0 and Δ. Prior to presenting the results of a calculation of the different terms, we note that for $T \to 0$ the homogeneous width converges to its (fluorescence) lifetime limited value.

Lyo[24] has recently calculated the second term in Eq. (11) (UPS contribution to $\Delta\omega_h$) by making the following assumptions:

$$\rho(\omega) = A\omega^a, \tag{12a}$$

$$\left\langle\int d^3r\,\Gamma(\omega,T)(1+e^{\hbar\omega/kT})^{-1}\right\rangle = \int_{r_{\min}}^{R_c} d^3r(n+1)(1+e^{\hbar\omega/kT})^{-1}\langle\Gamma(\omega)\rangle, \tag{12b}$$

where $n = (e^{\hbar\omega/kT}-1)^{-1}$ and $\langle\Gamma(\omega)\rangle = B\omega^3$, as derived by Anderson *et al.*[21] The decoupling approximation made by Lyo in condition (12b) is consistent with the assumption $\Delta \gg V$, which was made in this paper.

$$\begin{aligned}\delta(R_c) = \left|\frac{2\Delta}{E}(V_f - V_g)\right| &= CR_c^{-m}\\ &= (n+1)(1+e^{-\hbar\omega/kT})\langle\Gamma(\omega)\rangle\end{aligned} \tag{12c}$$

which is the exchange condition. The index f denotes the upper electronic state of the transition under consideration. In Eq. (12c), m is determined by the nature of the interaction between the molecule and a TLS. For a dipolar interaction $m = 3$, etc.

With these assumptions it is easily calculated that

$$\langle\langle[\pi T_2(T)]_u^{-1}\rangle\rangle = \alpha_u^m(kT)^{1+a+3(m-3)/m}. \tag{13}$$

Using the same set of assumptions we have calculated the third term (exchange contribution) in Eq. (11) and find also that

$$\langle\langle[\pi T_2(T)]_e^{-1}\rangle\rangle = \alpha_e^m(kT)^{1+a+3(m-3)/m}. \tag{14}$$

For the total homogeneous width we therefore find

$$\Delta\omega_h(T) = (2\pi\tau_{fl})^{-1} + (\alpha_u^m + \alpha_e^m(kT)^{1+a+3(m-3)/m}, \tag{15}$$

where α_u^m and α_e^m are the fractional contributions of the UPS and exchange mechanism to the temperature dependence of $\Delta\omega_h(T)$.

For a (static) dipole–dipole coupling between the optically active molecule and a TLS ($m = 3$, *vide infra*) and $r_{\min} = 0$ (as taken by Lyo) we find $\alpha_e^3/\alpha_u^3(r_{\min}=0) = 0.15$. When $r_{\min}$ becomes a sizable fraction of R_c this ratio will go up. We therefore conclude that UPS and exchange both contribute to the homogeneous width of an optical transition in an amorphous host. Furthermore, for $m = 3$ the homogeneous width has the following simple form:

$$\Delta\omega_h = (2\pi\tau_{fl})^{-1} + (\alpha_u^3 + \alpha_e^3)(kT)^{1+a} \tag{16}$$

showing that for a dipolar interaction the only factor determining the homogeneous width is the density of states function of the TLSs. Note further, that (only) for $m = 3$ the homogeneous width is independent of the frequency dependence of the tunneling lifetime $\Gamma^{-1}(\omega)$.

EXPERIMENTAL

Samples of pentacene in PMMA were obtained by pressing a mixture of PMMA grains and crystalline pentacene (Fluka) in a template on a hydraulic press at 200 °C. After rapid quenching, samples of good optical quality were obtained. Sample thickness was 1 or 2 mm, with a pentacene concentration of 4×10^{17} cm^{-3} (7×10^{-4} M), resulting in an absorption of 80% at 581.5 nm. Since the samples exhibited rapid decolorization under ambient light conditions they were stored in the dark at liquid nitrogen temperatures.

For most experiments the samples were mounted in a temperature-variable conduction-type cryostat built by Oxford Instruments. For some studies on heat dissipation at relatively high incident laser powers we used an immersion cryostat.

Accumulated photon echo experiments were performed as described in Ref. 31. Temporal resolution, as determined by the autocorrelation width, was 6 ps. Total incident laser power on the sample was 300–400 μW, and it was verified that at lower power levels the echo decay time was unchanged. Echo experiments were performed at several wavelengths between 5790 and 5840 Å using the laser dye rhodamine 6G. All showed the same decay time.

For the hole-burning experiments the bandwidth of the sync-pumped dye laser was reduced to less than 0.1 cm^{-1} by insertion of a thin (Spectra Physics High Free Spectral Range) and a thick (3 mm quartz plate) etalon. Under these

conditions the pulse correlation width increased to 132 ps. Absorption spectra of the hole were measured using a halogen lamp as an excitation source. The relevant portion of the spectrum was filtered out by a combination of glass and interference filters. The transmission through the sample was analyzed by a Spex 1402 double monochromator. Overall resolution, as limited by the convolution of laser and monochromator bandwidth, was determined to be 0.15 cm^{-1}. All hole widths cited in this paper were obtained after deconvolution of this contribution. The relevant power levels and irradiation times are discussed in connection with the data.

We finally note that the reported hole widths were measured, up to 8 K, after burning and reading at the same temperature[13(c),32] and for higher temperatures by burning at the lowest temperature (1.5 K) and measurement of the hole width at higher temperature. This latter procedure was chosen for the higher temperature measurements as the holes burned with the burn-read cycle at the same temperature became too broad. Both methods were found to yield identical results below 8 K provided the proper deconvolution is made.[32]

RESULTS

Absorption and emission spectrum of pentacene in PMMA

Figure 2 shows the optical absorption spectrum of pentacene in PMMA at 1.5 K. While in a mixed crystal of pentacene, e.g., in benzoic acid[7] the optical spectrum exhibits many sharp (1 cm^{-1}) vibronic features, in the polymer host the spectrum is devoid of any sharp structure, indicating a substantial inhomogeneous broadening in this host. The maximum of the origin intensity is found at 581.5 nm with an inhomogeneous width of about 300 cm^{-1}. The other broad feature in the spectrum at 536.2 nm is due to a pile-up of vibronic intensity in this region with an average frequency of the vibrational modes of 1450 cm^{-1}. To confirm the pentacene nature of the optical absorption spectrum the line-narrowed fluorescence spectrum was taken at the same temperature and is shown in Fig. 3. In contrast to the absorption

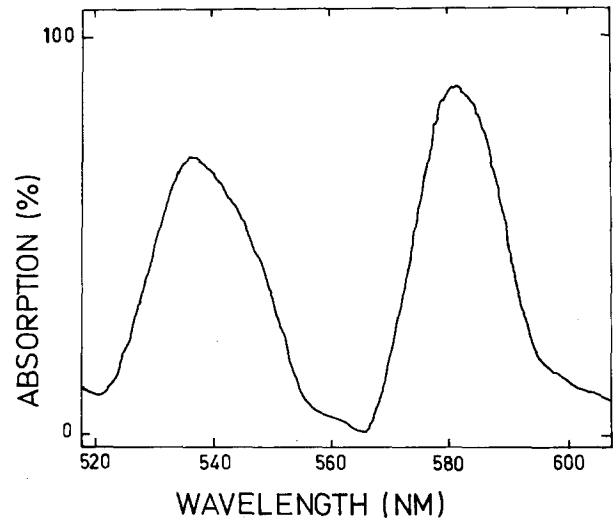

FIG. 2. Absorption spectrum of pentacene in PMMA at 1.5 K.

spectrum the laser induced fluorescence shows many sharp lines as excepted for a system with strong inhomogeneous broadening. The observed frequency intervals from the exciting laser frequency are furthermore in good agreement with those observed for pentacene in a crystal,[6] confirming the identity of the absorbing species as pentacene. Figure 3 further shows that the sharp vibronic features are accompanied by intense and broad phonon side bands signaling a much stronger coupling of the optical transition to the host polymer lattice than observed in a mixed crystal of pentacene. Further note that the Franck–Condon contour in emission very much resembles the one in absorption which supports the given interpretation of the broad absorption feature at 536.2 nm. Finally we wish to mention that the fluorescence lifetime of pentacene in PMMA was measured to be 14 ns which is somewhat shorter than the lifetime of pentacene in naphthalene. Referring to a previous publication of our group on the fluorescence lifetime of pentacene in different sites in *p*-terphenyl[33] we interpret the observed lifetime as a firm indication of an appreciable intersystem cross-

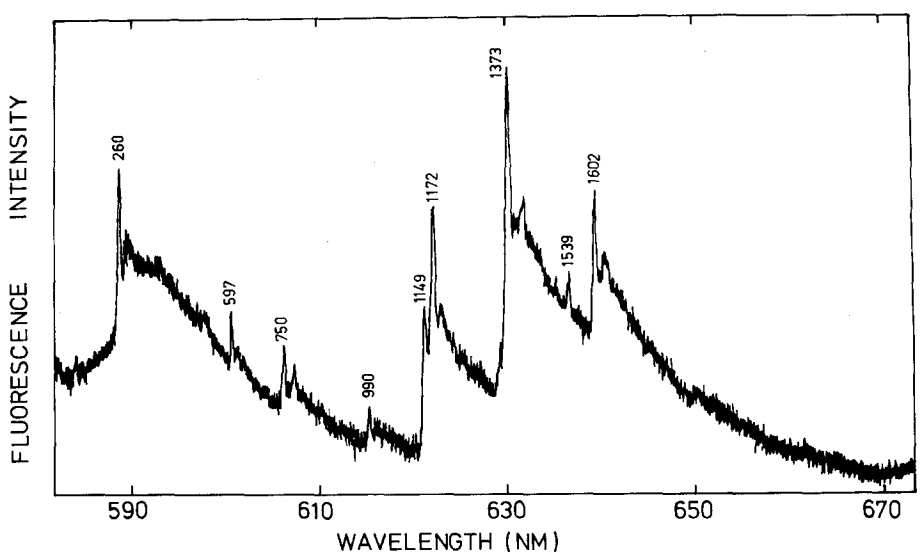

FIG. 3. Laser induced emission spectrum of pentacene in PMMA at 1.5 K. Excitation was in the origin region of the absorption spectrum at 5820 Å. The numbers above the lines give the energy of the vibration in wave numbers.

ing in pentacene in PMMA. This fact is of crucial importance to the possible application of the technique of the accumulated echo[31] to a study of optical dephasing in this system.

Accumulated photon echoes on pentacene in PMMA

In Fig.4 we show a trace of a decay of the accumulated photon echo[34] in pentacene in PMMA at 1.6 K. The solid line presents a fit to an exponential decay of the echo with a lifetime of 105 ps. We note that this echo decay is independent of the position in the inhomogeneous contour of the origin region implying that the mechanism of optical dephasing is site independent. The homogeneous width corresponding to this lifetime, $(\pi c T_2)^{-1}$, is 0.05 cm^{-1} which is about a factor of 10^4 smaller than the inhomogeneous width of the pentacene transition in this polymer. The (fluorescence) lifetime (τ_{fl}) contribution to the homogeneous width $[(2\pi c\tau_{fl})^{-1} = 0.0004\ cm^{-1}]$ at this temperature is therefore negligible, in contrast to the situation in mixed crystals where at this temperature the echo decay is lifetime limited. The temperature dependence of the echo decay constant is presented in a double logarithmic plot in Fig. 5 (lower curve). As the fluorescence lifetime over this temperature range does not change from its low temperature value of 14 ns its contribution to the homogeneous width remains negligible and the observed temperature dependence can be completely ascribed to a pure dephasing (T_2^*) effect. Moreover, since the double logarithmic plot yields a straight line we find no evidence for a residual linewidth larger than $(2\pi\tau_{fl})^{-1}$ as T approaches 0 K. The echo data can be fit to the following expression for T_2^*:

$$(\pi c T_2^*)^{-1}(T) = bT^{\beta}. \tag{17}$$

From a least square fit with this expression for T_2^* to the data we obtain $\beta = 1.30 \pm 0.05$ and $b = 0.0286 \pm 0.0014\ cm^{-1}$. It is interesting to note that exactly the same temperature dependence for optical dephasing was found for other molecules in the same polymer by the Voelker group[19] using the technique of photochemical hole burning.

We now turn to a discussion of the observed temperature dependence. In the Theoretical Background section we showed that the homogeneous width of an optical transition amidst a sea of TLSS has the form given by Eq. (15):

$$\Delta\omega_h(T) = (2\pi\tau_{fl})^{-1} + (\alpha_u^m + \alpha_e^m)(kT)^{1+a+3(m-3)/m},$$

where m is the order of the multipolar interaction and a the power of ω reflecting the TLS density of states. The constant in front of the temperature dependent part $(\alpha_u^m + \alpha_e^m)$ (b in our fit) is a measure of the average interaction strength between the molecule and the TLSS in the polymer. The exponent of T has a physically more transparent interpretation. Given a static dipole–dipole interaction ($m = 3$) for the coupling between pentacene and a TLS in PMMA (*vide infra*) one concludes from the observed $T^{1.3}$ temperature dependence of the homogenenous width that the TLS density of states (DOS) function in PMMA can effectively be represented as $\rho(\omega) = A\omega^{0.3}$. Data on the low-temperature heat capacity of PMMA[35] unfortunately show considerable scatter, but certainly allow for a fractional exponent for the (DOS) function with an argument of 0.3. In a number of inorganic glasses[36] a clear indication of a DOS function proportional to $\omega^{0.3}$ was obtained, suggesting that such a DOS may be a common feature of amorphous systems. It seems that careful measurements of DOS functions for amorphous organic systems would be extremely valuable considering the role they play in discussions of the various dephasing mechanisms.

For pentacene in PMMA it seems therefore that a *static* dipolar coupling mechanism is responsible for the observed

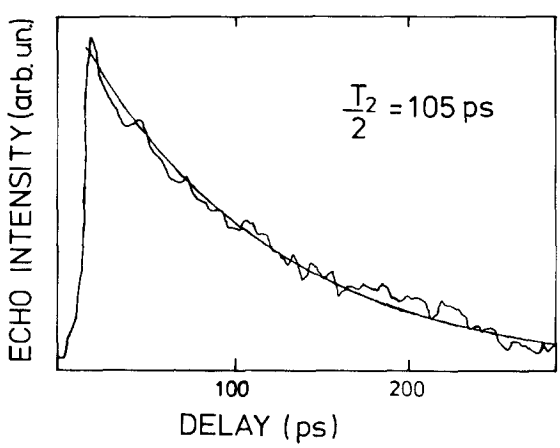

FIG. 4. Typical trace of a photon echo decay of pentacene in PMMA at 1.6 K. The solid line represents an exponential decay with a time constant of 105 ps. Laser wavelength here was 5815 Å: no effects on the decay time of laser wavelength were observed over the interval between 5790 and 5840 Å.

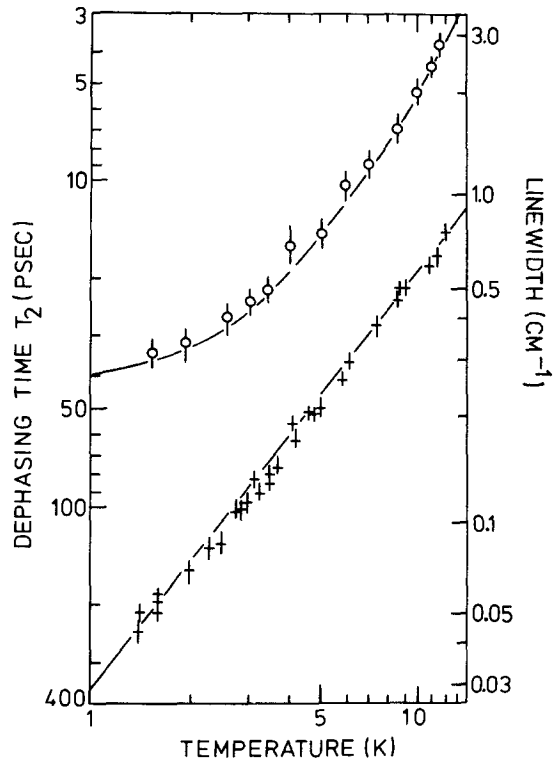

FIG. 5. Temperature dependence of the homogeneous linewidth of pentacene in PMMA. The lower curve (crosses) represents the photon echo data, the upper curve (open circles) depicts the "homogeneous" linewidth as inferred from nonphotochemical hole-burning experiments. The fits are discussed in the text.

dephasing. In a centrosymmetric site pentacene has no dipole moment; in an amorphous system, however, pentacene is located at a site without inversion symmetry and consequently can become polar. Recent Stark effect measurements on the centrosymmetric molecule perylene doped into polystyrene[37] show that the induced dipole can be quite substantial. On optical excitation a dipole moment change of no less than 7 D was measured.

One also expects a TLS system in PMMA to be also polar with the permanent dipole moment in the states of the double well being different. For different molecules in the same amorphous host one therefore expects b to be proportional to the change of the guests dipole moment on optical excitation.

When phonons stimulate a transition from one state to the other in a TLS system, the optical transition frequency, through the (static) dipolar coupling, is swept away, leading to dephasing of the transition. This *static* dipolar effect should not be confused with a recently proposed *dynamic* dipolar mechanism[30] for optical dephasing in a glass. This effect is negligible as the transition dipoles of a TLS and a molecule oscillate at completely different frequencies and are therefore decoupled.

We end this section with two remarks. First, that with the present dephasing theory, which relies on the presence of tunneling systems in amorphous materials, the TLS density of states should be a fractional power of the TLS frequency. We are not aware of calculations showing this to be an intrinsic property of amorphous solids. Second, that for the dephasing model presented, uncorrelated phonon scattering (UPS) and coherence exchange both contribute to optical dephasing. This result can be seen as a unification of the original proposal by Selzer *et al.*,[12] claiming exchange as the main source of dephasing in a glass and the recent suggestion by Lyo[24] that UPS was the only mechansim for dephasing in amorphous solids.

Hole burning and spectral diffusion

Hole burning, photochemical,[3,4,16,19] or nonphotochemical[1,2,13–15] has become a popular tool for measuring optical dynamics in solids. In photochemical hole burning a hole is burned in the absorption profile through a photoinduced (semi-) irreversible process like ionization, isomerization, or decomposition. These processes can occur with a high quantum yield ($1–10^{-2}$) and hole burning is efficient. In nonphotochemical hole burning it is the environment of the excited molecule which is changed through coupling of the excited species to degrees of freedom of the host. In glasses, nonphotochemical hole burning is thought to arise from photoinduced tunneling of molecules in the environment of the excited species. The efficiency of this process is often quite low (10^{-4}) and, in general, it therefore takes much more time (or power) to burn a hole. The width of the resulting hole therefore reflects the optical dynamics only if, on the time scale of the burning process, the fluctuation of the systems inhomgeneity is negligible. If this is not the case, hole burning does not measure the optical dynamics; instead spectral diffusion processes are measured. In this section we will show that nonphotochemical hole-burning experiments on pentacene in PMMA do not reflect the optical dynamics but rather probe spectral diffusion processes, as is apparent from a comparison of the hole burning results with the ones obtained from the accumulated photon echo experiments.

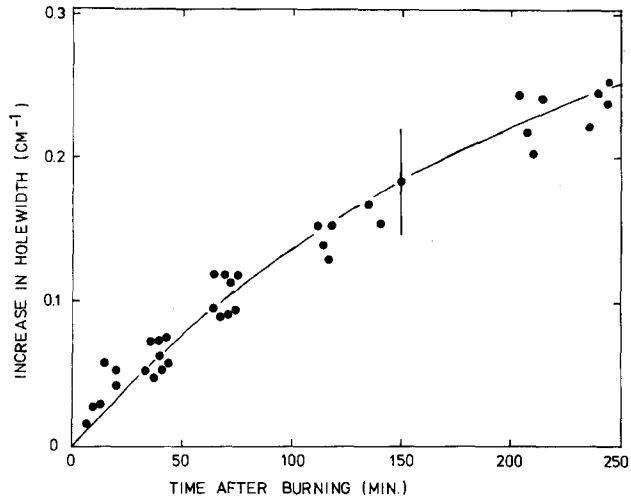

FIG. 6. Excess hole width as a function of time after burning at 1.5 K.

The results of this hole-burning study are given in Figs. 5 (upper curve) and 6. The narrowest hole, burned at 1.5 K, was 0.60 cm^{-1} broad, which transforms to a deconvoluted spectral width of 0.56 cm^{-1}. This hole was burned with the sample being cooled via conduction. Burning was achieved with a laser flux of 20 mW cm^{-2} for a period of 10 min. Longer buring times or higher incident powers resulted in broadening of the hole. In Fig. 5 the upper curve (open circles) represents the deconvoluted homogeneous linewidth of this hole.

Comparison of these data with the lower curve clearly indicates a significant discrepancy between the hole burning and the photon echo data. The solid line through the hole burning data is given by the expression

$$\Delta\omega = P + QT^2 \tag{18}$$

with $P = 0.28$ cm^{-1} and $Q = 0.019$ $cm^{-1}\,K^{-2}$. Equation (18) is functionally identical to what has been reported for the system quinizarine in boric acid.[16]

When hole burning was performed in an immersion-type cryostat the deconvoluted low temperature hole width reduced to 0.20 cm^{-1}, which is still a factor of 2 larger than the width predicted by the photon echo results. Excess broadening of the hole was now observed for laser flux greater than 10 mW cm^{-2} and irradiation times longer than 5 min. The temperature-induced broadening of the hole width up to 4.2 K, however, remained identical to what was observed in the conduction-type cryostat.

These experiments show that the effects of (laser) heating of the sample in a conduction type cryostat and, we suggest, also in a flow cryostat can substantially contribute to the low-temperature hole width. It is clear however that the *broadening* of the hole at higher temperature is due to a different process than the one that determines the photon echo decay.

To confirm that this other process is spectral diffusion we have looked at the hole width as a function of time after

burning. The results of this experiment are given in Fig. 6. One notes that, at the measuring temperature of 1.5 K, the hole broadens significantly on a time scale of hours, showing that slow rearrangement processes in the environment of the molecule take place. Of course, this experiment measures spectral diffusion with the probe molecule in the ground state. When the molecule is in its excited state (i.e., during burning) spectral diffusion may be enhanced. This could cause a larger hole width than the one expected from echo experiments in the bath cryostat where a linewidth of 0.2 cm^{-1} was observed even after the shortest burning time enabling hole measurements (~ 30 s).

Using the spectral diffusion theory of Klauder and Anderson,[38] as modified by Black and Halperin[39] to take the TLSs into account, we can fit the data of Fig. 6 to the following expression:

$$\delta[\Delta\omega(t)] = \delta[\Delta\omega(t\rightarrow\infty)](1 - e^{-2R_E t}) \qquad (19)$$

(valid only in the region $t \ll R_E^{-1}$) with the following constants: $\delta(\Delta\omega, t\rightarrow\infty) = 0.36^{-0.09}_{+0.18}\,cm^{-1}$; $R_E = 3.92^{+2.75}_{-1.77} \times 10^{-5}$ s^{-1}, where R_E is the energy-averaged maximum relaxation rate of the TLSs excited at 1.5 K. We therefore conclude that the temperature dependence of the hole width is also caused by spectral diffusion. Friedrich and Haarer's group[32,40] has recently also shown that spectral diffusion may have a marked effect on the widths of the holes obtained by nonphotochemical hole burning.

The precise form of the temperature dependence of the spectral diffusion process depends critically on the time scale of the experiment (τ_e) compared to inverse diffusion rate $(2R_E)^{-1}$. If $\tau_e \ll (2R_E)^{-1}$, then the hole width should be activated as T^4; in the other limit a linear-with-temperature increase of the hole width is expected. In our case $\tau_e \approx (2R_E)^{-1}$ and therefore an approximately quadratic temperature dependence is not inconsistent with this model. A linear-with-temperature hole width increase was observed by Hayes and Small[13(c),14] for tetracene in several organic glasses.

To conclude this section we wish to emphasize that comparison of the echo with the hole burning studies have shown that the time scale of the experiment selects the dominant mechanism for the measured spectral width. Amorphous systems are therefore intermediate between crystalline solids and liquids in the sense that the correlation time for the fluctuation of the forces that lead to what we call "inhomogeneous broadening" is short compared to that of a solid but very long compared to that of a liquid.

CONCLUSIONS

We have shown that the homogeneous width of a guest optical excitation in an amorphous solid can be understood if the excitation is coupled by dipole–dipole interactions to a random distribution of tunneling level systems (TLSs) with a density of states proportional to $\omega^{0.3}$. In a theoretical description of the homogeneous width a four level model, formed by coupling of the optical excitation to one TLS, can be used as a starting point. Optical Redfield theory may then be used to describe dephasing in this system after which the homogeneous width can be calculated by statistical averaging over a spatial distribution of TLSs. We show that next to a contribution from uncorrelated phonon scattering, the homogeneous width is also determined by effects of coherence exchange. We further conclude that our approach is equivalent to the Green's function method employed by Lyo.

We have also shown, by comparing the photon echo data with the results of nonphotochemical hole burning, that the hole width and its temperature-induced broadening are dominated by the effect of spectral diffusion.

As a final remark we wish to state that a critical test of the optical dephasing theory presented waits for a careful measurement of the density of states function of these low frequency TLS excitations.

Note added: As an amorphous solid is a space filling structure, its bulk topology cannot be described in terms of a fractal dimensionality. Very recently, however, Schilling[41] demonstrated that for chaotic (one-dimensional) configurations, as pertaining to glasses, the existence of TLSs can be proven theoretically, and, moreover, that it can be shown that these TLSs form a Cantor set of fractal dimension. Extension of this theory to three dimensions may very well be able to explain the ubiquitous $\omega^{0.3}$ density of states function for the TLSs that is proposed in the theoretical section of the present article.

Note added in proof: Dr. R. M. Macfarlane informed us that a similar discrepancy between homogeneous widths, as measured by photon echoes or by hole burning as reported in this paper was observed in the doped crystalline system $CaF_2:Pr^{3+}$ (Ref. 42). Here, spectral diffusion, due to slow nuclear spin flips, was shown to determine the width of holes burned in an absorption line.

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